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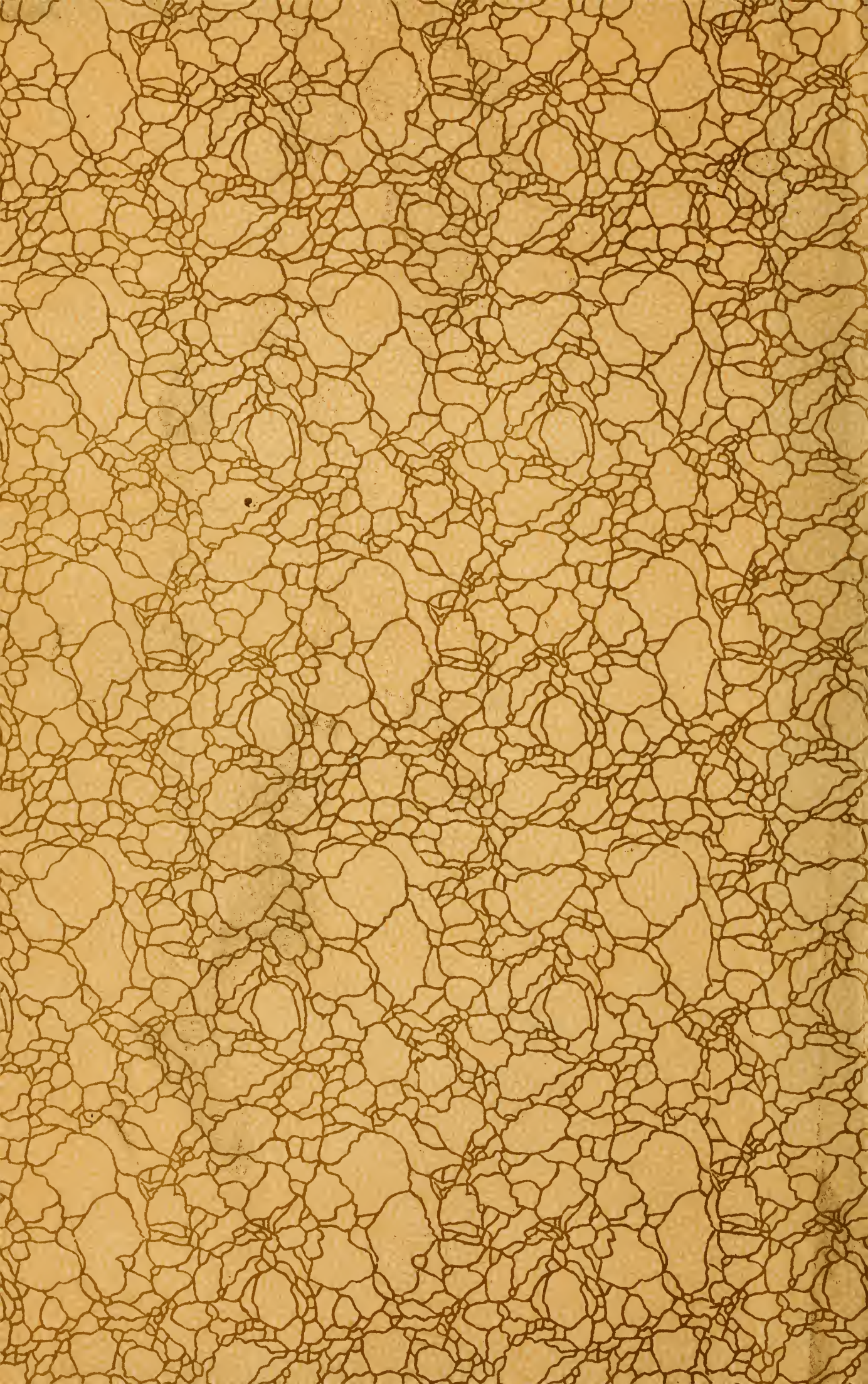


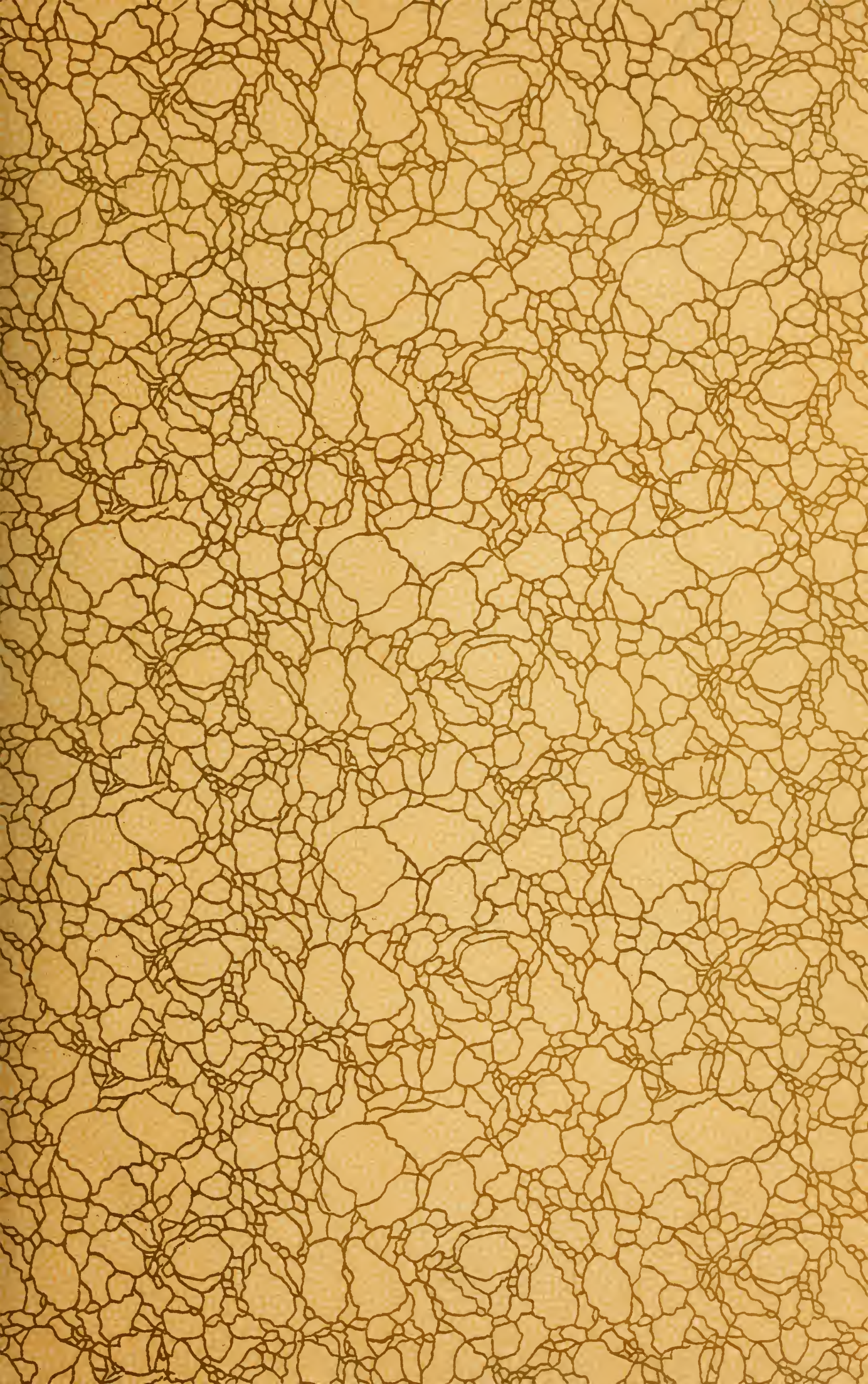
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THE THEORY OF THE HAMPSON LIQUEFIER.

By Edgar Buckingham.

1. **Introduction.**—The action of the Hampson or single-circuit type of liquefier involves the production of cold by the continuous expansion of gas within the liquefier from a high to a low pressure, and the conservation of cold by the Linde-Hampson regenerator, in which the nonliquefied cold gas is passed back over the copper inlet worm, thus giving up its cold to the high pressure gas which is advancing toward the expansion valve, and being itself warmed nearly to the temperature of the incoming gas. If the velocities of the feed and of the exhaust escaping from the regenerator are so small that the kinetic energy is negligible, as is usually the case in practice, the cold of expansion is due solely to the Joule-Thomson or porous plug effect.

The total cold available, per gram of gas fed in, is determined by the initial temperature θ_1 of the gas at the point where it enters the regenerator, its initial pressure p_1 , and the final pressure p_2 , which, in the Hampson liquefier, is one atmosphere. It can be computed if we know the specific volume and the rate of thermal expansion at constant pressure as functions of the pressure between p_2 and p_1 at the constant temperature θ_1 . It is independent of the internal construction or arrangement of the liquefier, of the distribution of temperature in the regenerator coil, and of all other circumstances whatever, provided, as stated above, that the kinetic energies of the feed and the exhaust are negligible.

This total cold available is used in the following three ways: (a) to offset the heat that leaks into the liquefier from outside, either through the insulation or along the copper worm; (b) to cool the whole quantity of gas from its initial temperature θ_1 to

the slightly lower temperature θ_3 at which the waste gas escapes from the regenerator; (c) to cool a fraction x of the gas from this exhaust temperature θ_3 to the normal boiling point θ_2 and there condense it into liquid, the cooling and condensation taking place at atmospheric pressure.

The thermal leakage depends on the particular construction of the liquefier and can not be computed *a priori*. The incompleteness of the regenerative process can be made negligible by increasing the interchanging surface; or its effect can be computed and allowed for. These two terms represent losses which reduce the fractional yield or efficiency of liquefaction, x . If we know the latent and specific heats of the gas, together with the above-mentioned data for computing the total cold available, we can compute the ideal value of x which would be attained if the thermal insulation were perfect.

It is easy to prove the correctness of these statements by elementary thermodynamics. This will be done in §§ 2 and 3, while in §§ 4 and 5 it will be shown that the results of computation agree satisfactorily with the published results of experiments on the efficiency of the Hampson liquefier.

2. The total Cooling Effect Available in a Completely Irreversible Expansion.—Suppose the machine to have been working so long that a steady state has been established. Let the resistance offered to the nonliquefied gas in escaping through the regenerator be so small that the pressure on the low pressure side of the valve is sensibly the same as the outside atmospheric pressure. Let the kinetic energy of the eddy currents formed at the valve be all dissipated into heat inside the liquefier—if the valve is replaced by a fine-grained porous plug, this kinetic energy is small and is dissipated within a short distance of the plug.

In Figure 1, let A , at (p_1, θ_1) , represent on the p, v plane the initial state of one gram of gas as it enters the regenerator coil.

Let B , at (p_2, θ_2) , represent the state of the same gas just after it has issued from the expansion valve, the kinetic energy of eddy currents being assumed to be already dissipated. This assumption simplifies the reasoning, but is not essential. The eddy currents may be dissipated anywhere before the waste gas escapes at the exhaust without affecting the final result, except in so far

as slight changes in the distribution of temperature inside the liquefier may influence the thermal leakage in from outside. If any liquefaction at all is taking place, θ_2 is the normal boiling temperature at atmospheric pressure p_2 , and at B the substance is a mixture of liquid and saturated vapor.

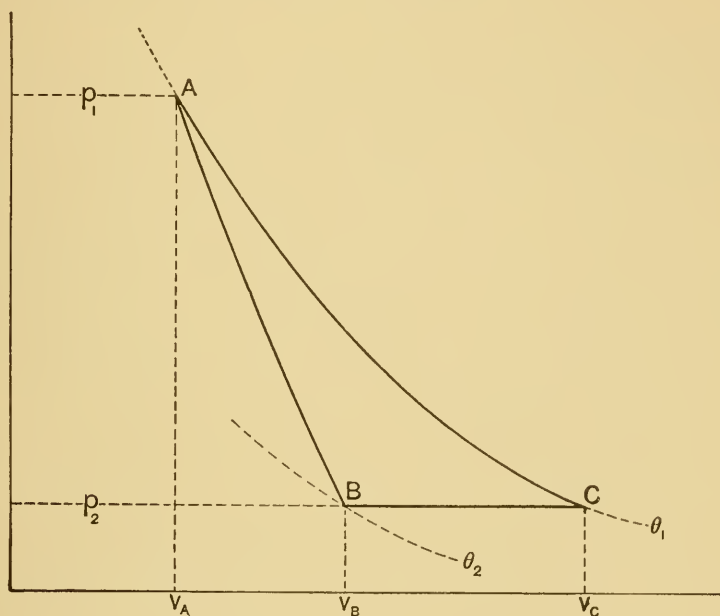


Fig. 1.

Let C , at (p_2, θ_1) , represent the state the gram of gas would have been in if, during the same fall of pressure through a porous plug or throttling valve, heat had been supplied so as to keep the temperature from changing.

Let Q_1 be this quantity of heat. Let Q_2 be the heat needed to convert the mixture of liquid and vapor at B into gas at C while the pressure remains constant at p_2 or one atmosphere. Let ϵ be the internal energy of one gram of the substance.

The work done by the compressor on the gram of gas as it enters the liquefier is $(pv)_A$; that done by the gas as it issues from the valve against the outside pressure p_2 is $(pv)_B$ at the temperature θ_2 , or $(pv)_C$ at the temperature θ_1 . We therefore have for the increase of internal energy during the isothermal process AC

$$\epsilon_C - \epsilon_A = (pv)_A - (pv)_C + Q_1 \quad (1)$$

For the adiabatic process AB , since no heat is supplied, we have

$$\epsilon_B - \epsilon_A = (pv)_A - (pv)_B \quad (2)$$

whence by subtraction and rearrangement we have

$$Q_1 = (\epsilon_c - \epsilon_B) + p_2(v_c - v_B) \quad (3)$$

the pressure p_2 being the same at B as at C , i. e., the adiabatic and the isothermal expansion having taken place between the same limits of pressure, so that $(pv)_c - (pv)_B = p_2(v_c - v_B)$.

Consider now the heat Q_2 needed to heat the mixture from B to C . This is equal to the increase of the internal energy or $(\epsilon_c - \epsilon_B)$ plus the external work done by the substance during this boiling off and warming up. The pressure being constant, this work is merely the pressure multiplied by the increase of volume, or $p_2(v_c - v_B)$. Hence we have

$$Q_2 = (\epsilon_c - \epsilon_B) + p_2(v_c - v_B) \quad (4)$$

Since by the first law of thermodynamics the difference in the internal energy of a system in any two states is dependent solely on the states themselves and not on how they are reached $(\epsilon_c - \epsilon_B)$ is the same however computed, so that equations (3) and (4) are equivalent to

$$Q_1 = Q_2 \quad (5)$$

We may interpret this result in words as follows: If we let the expansion through the valve take place isothermally at the initial temperature and then subsequently abstract from the expanded gas at this final pressure the same amount of heat that we had to put in during the isothermal expansion, the final state reached after this double process is the same as if we had let the expansion go on without supplying or withdrawing any heat at all, as is the case—except for the imperfect thermal insulation—in the operation of the Hampson liquefier.

The magnitude of this quantity of heat Q_1 , or the total cooling effect available per gram of gas, obviously depends only on the limits of pressure and on the initial temperature at which the expansion AC is supposed to occur and not on the details of anything that may happen inside the liquefier.

If we let ρ be the ratio of the heat absorbed by one gram of gas at θ_1 to its fall of pressure in expanding by an infinitesimal amount through a throttling valve or porous plug, with the kinetic energy of eddy currents all dissipated, we have—

$$\delta Q_1 = -\rho \delta p \quad (6)$$

whence

$$Q_1 = \int_{p_2}^{p_1} \rho dp \quad (\theta = \theta_1) \quad (7)$$

We also know that the quantity ρ , or the Joule-Thomson effect, satisfies the familiar equation¹—

$$\rho = \theta \left(\frac{\partial v}{\partial \theta} \right)_p - v \quad (8)$$

where θ is the absolute thermodynamic temperature. If we let v_0 be the specific volume at 0°C. , and $\alpha = \frac{1}{v_0} \left(\frac{\partial v}{\partial \theta} \right)_p$, we have by (7)

$$Q_1 = \int_{p_2}^{p_1} (\theta_1 \alpha v_0 - v) dp \quad (\theta = \theta_1) \quad (9)$$

Hence the total cold available per gram of gas fed into the liquefier may be found if we know the values of the coefficient of expansion α and the specific volumes v_0 and v at 0°C. and at θ_1 as functions of the pressure. It is, of course, not necessary to express these functions by equations; it suffices to plot the values of $(\theta_1 \alpha v_0 - v)$ as ordinates against p as abscissa, draw a smooth curve through the points, and find the integral between any two pressures by taking the area under the curve and between the two pressures in question.

3. Efficiency of the Hampson Process.—Let x be the fraction of the gas fed in that remains finally as liquid. Let θ_3 be the temperature of the exhaust escaping from the regenerator. Let L be the latent heat of the boiling liquid and C_p the specific heat of the gas, both at the constant pressure of one atmosphere.

¹ Kelvin Papers Vol. I, p. 428. See also Phil. Mag. (6), 6, p. 518, 1903; and note at the end of the present paper.

The resulting product, at B (Fig. 1), of the actual expansion of one gram of gas fed in is a mixture of x grams of liquid and $(1-x)$ grams of gas. To evaporate the liquid and warm the resulting gas up to θ_3 would require a quantity of heat

$$x(L + \int_2^{\theta_3} C_p d\theta)$$

To warm the $(1-x)$ grams of gas from θ_2 to θ_3 requires no heat *from outside*, for this heat is supplied in the regenerator by more gas, which has already entered the liquefier. The whole gram of gas has now to be heated further, at p_2 , from θ_3 to θ_1 , which requires a quantity of heat

$$\int_{\theta_3}^{\theta_1} C_p d\theta$$

Let H be the heat that leaks in from outside per gram of gas fed in, the whole process being in fact not quite adiabatic. Then the total heat that would have to be supplied from outside, including H , to get the resulting product at B (Fig. 1) back to C is

$$Q_2 = x(L + \int_{\theta_2}^{\theta_3} C_p d\theta) + \int_{\theta_3}^{\theta_1} C_p d\theta + H \quad (10)$$

By comparing this with (5) and (9) we have

$$x = \frac{\int_{p_2}^{p_1} (\theta_1 \alpha v_0 - v) dp - \int_{\theta_3}^{\theta_1} C_p d\theta - H}{L + \int_{\theta_2}^{\theta_3} C_p d\theta} \quad (11)$$

The specific heat of air at one atmosphere is very nearly constant to at least as low as -170°C . If therefore we set $C_p = \text{constant}$, we have as a sufficient approximation for purposes of computation

$$x = \frac{\int_{p_2}^{p_1} (\theta_1 \alpha v_0 - v) dp - C_p(\theta_1 - \theta_3) - H}{L + C_p(\theta_3 - \theta_2)} \quad (12)$$

In these equations, the denominator is the "total heat" of one gram of the substance from liquid at its normal boiling point to

gas at the temperature of the exhaust. Hence the physical meaning of the right-hand side of the equations is clear. The first term is the total cold per gram fed in divided by the cold needed to liquefy one gram, i. e., it is the fraction of the gas that will be liquefied if there is no waste. The second term is the cold wasted by imperfect regeneration, divided by the same denominator, i. e., it is the liquid wasted, per gram of gas fed in, on account of the insufficiency of the regenerator surface. The third term, in like manner, is the liquid wasted on account of the lack of perfect thermal insulation.

This last term can not be computed in any general way. We may, however, say that starting with small rates of feed its importance at first decreases as the rate of feed increases, for the total thermal leakage will not increase so fast as the total rate of flow of gas into the liquefier. Hence the leakage per gram will decrease. Leaving this term out of account we have remaining only quantities on which we have some numerical data for air and hydrogen, and we may use the equation

$$x = \frac{\int_{p_2}^{p_1} (\theta_1 a v_0 - v) dp - C_p (\theta_1 - \theta_3)}{L + C_p (\theta_3 - \theta_2)} \quad (13)$$

for computing x in specific cases. If the regenerating surface is so large that the exhaust has risen sensibly to the temperature of the feed, we have $\theta_3 = \theta_1$ and the last term vanishes, leaving for the ideal case of perfect regeneration and perfect insulation

$$x = \frac{\int_{p_2}^{p_1} (\theta_1 a v_0 - v) dp}{L + C_p (\theta_1 - \theta_2)} \quad (14)$$

4. Application to Air at 16° C.—According to Witkowski² the specific heat of air from +100° C. to -170° C. appears to be about 0.237 calories per gram with, possibly, a slight increase at the lowest temperatures. We shall be close enough to the true value if we take 0.24 or, setting $J = 42 \times 10^6$, $C_p = 1.01$ [joules/gram].

² Phil. Mag. (5), 42, p. 1, 1896.

The latent heat of boiling air depends, of course, on the composition of the liquid and is somewhat uncertain. The experiments of Behn, Shearer, Estreicher, Richtmeyer, and Alt indicate a value of about 50 calories per gram, so that we shall take $L = 210$ [joules/gram].

Taking θ_2 , the boiling point at one atmosphere, to be $-191^{\circ}.5$ C. or $81^{\circ}.5$ K³ we have for the total heat of 1 gram of liquid air up to the exhaust temperature

$$L + C_p (\theta_3 - \theta_2) = 210 + 1.01 (\theta_3 - 81.5)$$

which gives us the denominator of equation (13) when θ_3 is known.

For the specific volume and coefficient of expansion we have data by Witkowski⁴ at several temperatures and up to 130 atmospheres. We have also data by Amagat⁵ up to very much higher pressures. Witkowski's data have been preferred because they are given in much greater detail. From 130 atmospheres up to 200 atmospheres Amagat's data have been used to guide the extrapolation of Witkowski's values.

We may illustrate the use of equation (13) by the data for air at 16° C. It is needless to give the details of the computation of the Joule-Thomson effect, but the results are shown in Fig. 2 in which the abscissas are pressures in atmospheres and the ordinates the values of the Joule-Thomson effect, the unit of $(\rho \times p)$ being $(1 \text{ atm.} \times 1 \text{ cm}^3)$ or 0.1013 joules, and the unit of mass being 0.001293 gram. The values deduced from Witkowski's data are marked by crosses. At low pressures, ρ appears as a small difference of two large quantities and is therefore subject to large errors. To help out, we have the value determined by Joule and Thomson by direct experiment for various low pressures. This value is marked by a circle.

Curve A has been drawn to represent $\rho = f(p)$. From 50 atmospheres down it is drawn somewhat arbitrarily, but the uncertainty in the total area is not great. These experimental values lie sur-

³The symbol K (Kelvin) is used to denote the thermodynamic absolute scale of temperature.

⁴Phil. Mag. (5), 41, p. 288, 1896.

⁵Ann. de Ch. et Phys. (6), 29, p. 68, 1893.

prisingly close to curve *B*, which shows what the Joule-Thomson effect would be at 15°.6 C., if the air followed van der Waals's

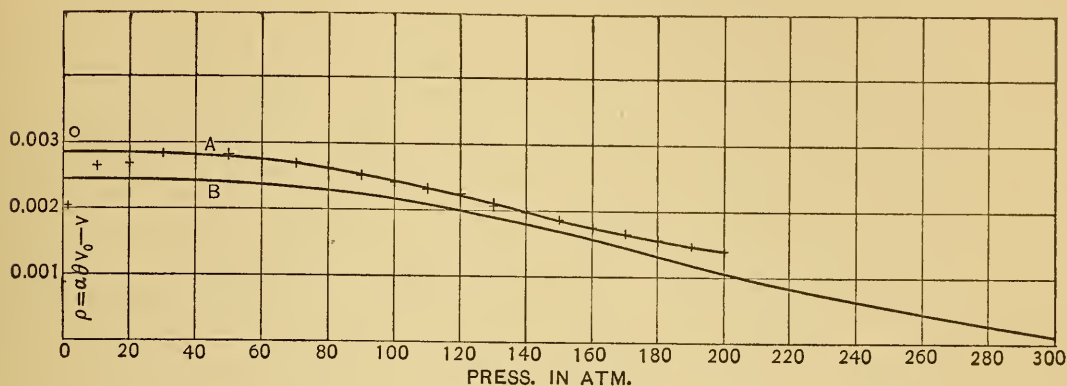


Fig. 2.

equation and had the critical constants $\theta_c = 133^\circ \text{ K}$, $p_c = 39.3 \text{ atm.}$, $v_c = 2.85 \text{ cm}^3/\text{gm.}$

From curve *A* we can find the value at 16° C. or $\theta_1 = 289^\circ \text{ K}$ of

$$\int_{p_2}^{p_1} (\theta_1 a v_0 - v) dp \text{ between any two pressures up to 200 atmos-}$$

pheres. We can then, after reducing the values to joules per gram, substitute them in equation (13), together with the values of C_p and L already given. We thus get the value of the efficiency x for any initial pressure, up to 200 atmospheres, and for any value of the exhaust temperature, θ_3 , the thermal insulation being assumed to be perfect.

The resulting values of x are plotted in Fig. 3. Curve *A* is computed for $\theta_3 = \theta_1$, i. e., for perfect regeneration. Curve *B* is computed for $\theta_3 = \theta_1 - 5^\circ$. The change in x caused by small changes in $(\theta_1 - \theta_3)$ is nearly linear, as may be seen from equation (13), so that the value of x for any other small value of $(\theta_1 - \theta_3)$ may be found from these two curves by linear interpolation or extrapolation.

5. Comparison of Computed with Observed Values of x .—It is interesting to compare the computed values as shown by the curves of Fig. 3 with the values observed by Messrs. Bradley and Rowe.⁶ All but three of their experiments were made at an initial

⁶ Phys. Rev. 19, p. 330, 1904.

temperature of about 2°C . or $\theta_1 = 275^{\circ}\text{K}$. It would thus have been better to compute the values of x for this temperature, but data were lacking, so that 16° has been used. There are, in all, ten experiments at about 181 atmospheres initial pressure, and six others at various lower pressures. To be comparable with the computed values these observations have to be reduced.

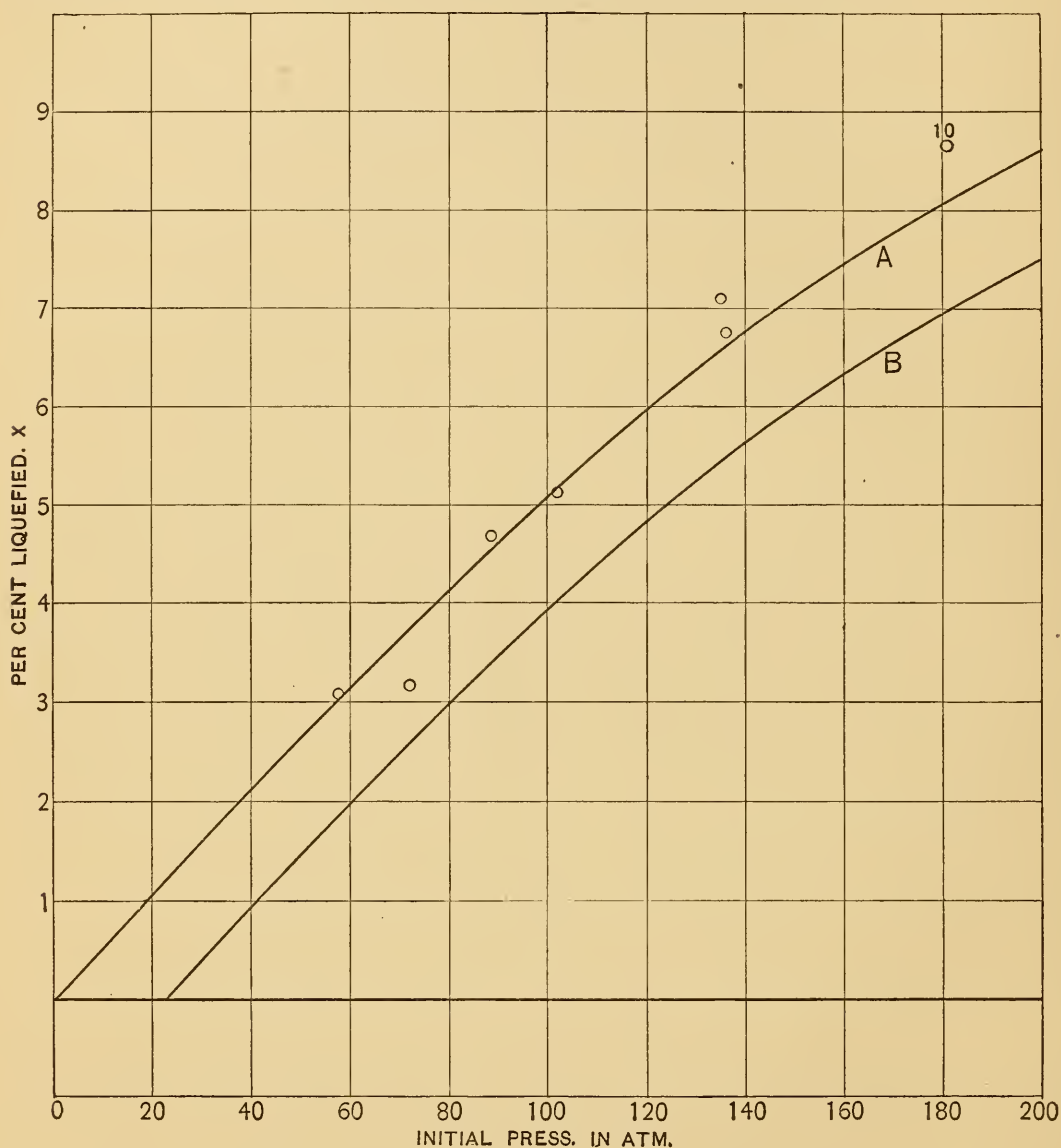


Fig. 3.

In the first place, the insulation of Messrs. Bradley and Rowe's liquefier was, of course, not perfect. To correct for this I have assumed that within the comparatively small variations of flow

used, the temperature gradients were not sensibly altered by changes in the rate of flow, so that the total heat leakage inward was the same in all cases, and therefore that the amount of liquid wasted per gram of air fed in, or the decrease in x due to thermal leakage, was inversely proportional to the rate of feed. Letting x be the observed value, x' the value that would have been observed if the insulation had been perfect, M the rate of flow, and A the decrease of x by thermal leak when the flow is unity, we have

$$x = x' - \frac{A}{M}$$

The value of A was found from the three, presumably strictly comparable, experiments made with special reference to the influence of varying rate of flow. Its mean value, when x is given in per cent and M in cubic feet per minute, is 20.6, so that we have as our reduction formula

$$x' = x + \frac{20.6}{M}$$

All the observed values of x have thus been corrected for the effect of thermal leak. They are shown in Table I, Column VI.

In the experiments at 181 atmospheres, the temperature of the exhaust was always very near that of the feed, so that the regeneration was sensibly perfect and no correction is needed on this score. At the lower pressures, however, the exhaust was colder than the feed. The necessary correction was found by linear interpolation between curves *A* and *B* of Fig. 3 and the values of x with this second correction applied are given in Column VII of the table. The sixteen values in this column are therefore, as nearly as we can compute them, the results which would have been obtained if the thermal insulation had been perfect and the regenerator surface large enough for perfect heat interchange even at the low pressures where the linear velocity of the air through the worm was greatest.

But these values still all refer to an initial temperature of about 2° C. We have finally to reduce them to 16° before comparing with the computed curve *A* of Fig. 3. To do this, we plot the

results of the four experiments made at $p_1=180$ atmospheres and at initial temperatures of 2° , 30° , 59° , and 92° C. When the observed values of x are corrected as above for thermal leak and plotted against θ_1 , they lie on a smooth curve. The ratio of the ordinate of this curve at 16° to that at 2° is 0.87. I have assumed that the ratio would have been the same if the pressure p_1 had been different from 180 atmospheres, and have reduced the corrected values of x for 2° to 16° by multiplying them by 0.87.

TABLE 1.

Summary of Observations by Bradley and Rowe.

I	II	III	IV	V	VI	VII	VIII
Ref. to Phys. Rev., vol. 19 pp.	p_1 (atmosph.)	M (ft. ³ per min.)	\bar{x} observed	$\theta_1-\theta_3$	\bar{x} corr. for thermal leak	\bar{x} corr. for ($\theta_1-\theta_3$)	$0.87 \bar{x}$ = \bar{x}_{16}
335	181.3	14.9	8.6	0.00	9.98	9.98
335	180.3	15.5	8.0	0.00	9.33	9.33
335	180.3	14.4	8.1	0.00	9.53	9.53
335	181.0	15.0	8.7	0.00	10.07	10.07
335	181.6	13.6	8.8	0.00	10.32	10.32
339	181.3	14.9	8.6	0.00	9.98	9.98
339	180.3	14.4	8.1	0.00	9.53	9.53
341	180.3	13.6	8.8	0.00	10.31	10.31
341	180.3	10.8	8.3	0.00	10.21	10.21
341	180.3	8.1	7.8	0.00	10.34	10.34
.....	180.7	9.96	8.67
339	136.1	15.8	6.4	0.25	7.70	7.76	6.76
339	102.0	16.2	4.5	0.50	5.77	5.89	5.13
339	72.0	17.1	1.7	3.25	2.90	3.65	3.18
339	134.7	14.6	6.5	1.0	7.91	8.14	7.09
339	88.4	15.8	3.5	2.5	4.80	5.37	4.68
339	57.8	16.4	1.0	5.5	2.26	3.52	3.07

There are evidently some rather uncertain assumptions involved in this reduction as well as in the correction of observations at very different initial temperatures for thermal leakage; but it is the best we can do, and it is better to base the reduction on the

internal evidence of the work of Messrs. Bradley and Rowe than to use any formula, theoretical or otherwise, deduced from other and independent *a priori* considerations. The ten observations at 181 atmospheres have been averaged before reduction, so that we have in Column VIII of the table seven values which are, as nearly as we can tell, what would have been obtained at an initial temperature of 16° C., and the various initial pressures, under ideal conditions of insulation and regeneration. These seven points are plotted in Fig. 3 surrounded by circles.

When we remember that all the points except that marked 10 represent single experiments, we must, in view of the unavoidable experimental errors in x which may be estimated from the first ten values in Column VII of the table, consider the agreement of the observed and computed values to be sensibly perfect up to about 130 atmospheres, the upper limit of Witkowski's experimental data. The point marked 10, representing the mean of ten experiments, lies distinctly above the curve, which is here based on extrapolated data and may be too low, the probable error of the mean of the ten experiments computed in the usual way being only 0.08 while the curve passes about 0.5 below the point.

It has thus been shown, in the specific case of the best set of experimental values available, that the observed values of the efficiency or ratio of liquefaction x , when so reduced as to be comparable with values computed *a priori* from experiments on the properties of air at ordinary temperatures or at atmospheric pressure, do agree quite well with the computed values, so far as the latter can be considered reliable. We may congratulate ourselves on finding that none of the existing data we have had to use seem to be far wrong, in spite of their heterogeneous nature and the great experimental difficulties involved in obtaining them, especially in such work as that of Witkowski.

6. Methods of Increasing the Yield.—It has been shown that if the regenerator surface is large enough, the internal arrangement of the liquefier can influence the liquefaction ratio only in so far as it may influence the temperature gradients which determine the thermal leakage and the resulting waste of liquid. If a given liquefier has sufficient regenerator surface, the only thing that can be done to improve its yield, when fed with air at a given

pressure and temperature and at a given rate, is to improve the thermal insulation. The experiments of Messrs. Bradley and Rowe show, in agreement with equation (12), that the fractional yield or efficiency of liquefaction increases with the rate of feed. The most obvious improvement in operation is therefore the use of a larger compressor and higher rate of flow. There is a limit to this, however, for a point will be reached where the regenerator surface becomes so insufficient and the low temperatures are brought so near the inlet end of the coil that the losses offset the gains.

A second method of improving the yield, with a given mass of air passing per second, is to use higher initial pressures. At 16° C. the Joule-Thomson effect is about half as great at 200 atmospheres as at low pressures, to judge from the curve representing Witkowski's experiments, but there is still some advantage to be gained by increasing the initial pressure. How far this would continue we can not say, for we have no sufficient data; but from curve *A* of Fig. 2 it seems likely that ρ would pass through zero somewhere in the vicinity of 400 atmospheres, and that the total increase of available cold attainable by increasing the initial pressure to this point would be only about one-third of what we already have at 200 atmospheres. Amagat's observations at 0° and 15° 7 also indicate that for a mean temperature of 7° 85 the inversion pressure would be close to 400 atmospheres.

Curve *B* of Fig. 2, computed from the reduced van der Waals equation

$$\left(p + \frac{3}{v^2}\right)(3v - 1) = 8\theta$$

together with the critical constants already quoted, crosses the axis at 328 atmospheres. The curve computed from the equation

$$\left(p + \frac{3}{\theta v^2}\right)(3v - 1) = 8\theta$$

crosses the axis at 268 atmospheres but does not pass anywhere near the experimental points shown by the crosses in Fig. 2, being everywhere very much lower. A similar curve computed from the equation

$$\left(p + \frac{16}{3\theta v^2}\right)(4v - 1) = \frac{128}{9}\theta$$

deduced by D. Berthelot⁷ for low pressures, lies close to curve *B* up to 80 atmospheres, but thereafter falls much less rapidly than *A* or *B* and crosses the axis at about 770 atmospheres. Up to 200 atmospheres the simple van der Waals equation seems to represent the facts fairly well and it is the best guide we have in guessing at what may happen outside the range of the available experimental data.

The third and most effective way to increase the yield of a given liquefier is to use precooling, i. e., to lower the initial temperature θ_1 at which the air enters the regenerator. That this gives a rapid increase of efficiency is shown for temperatures between 0° and 100° by the experiments of Messrs. Bradley and Rowe as well as by Joule and Kelvin's porous plug experiments. For lower temperatures we have only rather scanty data, but from Witkowski's figures, treated as before, we find, for air at an initial pressure of 130 atmospheres, the following ideal maximum values:

$t_1 = +16^\circ \text{C.}$	-35°C.	$-78^\circ.5 \text{C.}$
$x = 6.3 \text{ per cent.}$	9.2 per cent.	14.4 per cent.

Similarly for hydrogen,⁸ with an initial pressure of 60 atmospheres we find

$t_1 = -190^\circ \text{C.}$	-212°C.
$x = 8.3 \text{ per cent.}$	16.2 per cent.

These values are based on imperfect data, but doubtless give an approximate idea of the advantage to be gained by precooling.

Whether there is any corresponding increase in the mechanical efficiency, i. e., in the amount of liquid produced per kilowatt hour expended, is another question into which I shall not enter here. In general laboratory practice, energy is usually the cheapest of the things used and the problem is commonly how to get

⁷ Trav. et Mem. Bur. Int. Vol. XIII.

⁸ Witkowski: Bull. Cracow Ac. Sc., June, 1905.

liquid as fast as possible from the apparatus available, regardless of how much power is used. The whole problem of the mechanical efficiency of the Hampson or the more complicated Linde process could be treated by the principles already set forth so far as data on the thermal and mechanical properties of the gas to be liquefied are at hand.

7. On Dissipation at the Valve.—It is sometimes said or implied that friction at the valve is a source of loss of efficiency because heat is thereby generated, but this is a misconception if we are considering only the Hampson or Linde process.

The truth of this statement is most easily seen by considering extreme cases. Suppose the valve to be replaced by a nozzle designed, as in the case of a steam turbine nozzle, so as to allow the flow to be as smooth and free as possible. We shall now have a very high exit velocity with high kinetic energy. This kinetic energy represents a decrease in the internal energy of the gas as it expands and the gas *in the jet* is cooled a great deal. But if all this kinetic energy, except the small amount corresponding to the velocity needed to carry the exhaust away quietly through the regenerator, is dissipated *inside the liquefier*, the total result is precisely the same as if we went to the opposite extreme and used a very fine-grained porous plug so as to have almost no kinetic energy at all in the issuing gas. The result is the same in any intermediate case; with a high velocity of escape from the nozzle or valve, we get very great local cooling but an equivalent heating somewhere else. There is a definite total amount of cold available inside the liquefier, and if we get more at one place and so liquefy a higher percentage of the gas in the jet as it issues from the valve, we have to pay for it somewhere else, for we are developing an equivalent amount of heat somewhere else *inside* the liquefier. If we avoid dissipation at the valve by the use of a well-designed nozzle, and then convert the resulting kinetic energy, not into heat but directly into work which we lead out along a turbine shaft, we may get a highly increased efficiency. But we are then introducing a new source of cold and making a radical change in the principle of the liquefying process. This dissipation of energy inside the liquefier is an essential characteristic of

the completely irreversible expansion occurring in the Linde or Hampson process. Gas enters the apparatus by one opening at high pressure while the work done on it in forcing it in is the product of its volume by the high pressure. It issues by another opening doing work equal to the product of its new volume by the new pressure. The total heating or cooling effect is the sum of two independent parts, one due to the fact that the product (pv) changes with the pressure and the other to the fact that the internal energy also changes with the pressure. We have the resultant of external and internal work, both of which are zero, by definition, for the ideal gas, but may be either positive or negative in any other fluid, whether liquid or gas. The energy that is dissipated inside the liquefier is what might be obtained as work if the expansion could be carried out reversibly, instead of irreversibly.

If by the use of a motor, as in Claude's process,⁹ part of this work can be saved from dissipation inside the liquefier, the available cold and the amount of liquid produced are increased correspondingly. In either case, the Joule-Thomson effect remains the same. In the completely irreversible plug expansion, that is the only source of cold; in the other case there is an added source of cold in the abstraction of energy by the motor.

At an initial temperature of 16° C. and pressure of 40 atmospheres, insulation and regeneration being perfect, the amount of air liquefied with completely reversible expansion would be about 23 per cent instead of the 2.1 per cent attainable by the completely irreversible liquefier of the Hampson type.

8. Liquefaction before the Valve.—Although it seems sufficiently proven that the internal arrangement of the Hampson type of liquefier influences the yield only in so far as it influences the losses due to thermal leakage and imperfect regeneration, there is one more point that may be worth considering.

It has been found experimentally¹⁰ that if the last few turns of the coil are immersed in the liquid air produced, the net yield is

⁹ Journ. de Phys. (4) **5**, p. 1, 1906.

¹⁰ Cottrell; Journ. Phys. Chem. **10**, p. 265, 1906.

Bradley and Fenwick; *ibid.*, p. 275.

precisely the same as with the more usual arrangement where the valve is at the lowest point of the coil. In the ordinary case, the air when it reaches the valve is probably above its critical temperature of -140°C . At all events, if the pressure is as high as 100 atmospheres and no precooling is used, the temperature to which the advancing air can be cooled by the action of the regenerator is very considerably above -140°C ., although some further cooling may take place by conduction back from the valve along the worm. Assuming, then, that the air is above its critical temperature, it is naturally looked upon as a gas. When the last few turns of the worm are immersed in liquid air it may be assumed as highly probable that the air reaches the valve below its critical temperature. Hence we may naturally look upon it as a liquid in view of its high pressure. The distinction is in reality only a matter of definition, for so long as a fluid is subject to more than its critical pressure, no liquefaction in the sense of a separation into liquid and gaseous phases can ever take place, no matter how low the temperature may be.

After what has been said above regarding the method of computing the efficiency of liquefaction, this experimental result is not surprising. The view has, however, been expressed, that since the air reaching the valve is already liquid, the Joule-Thomson effect must be very small or zero, and the conclusion has been drawn that some other and unfamiliar source of cooling must come into play. This conclusion is unnecessary, for there is no sufficient reason for assuming that the Joule-Thomson effect is either negligible or small under the given conditions. The Joule-Thomson effect is a property not of gases alone, however the gaseous state may be distinguished from the liquid, but of all fluids or fluid mixtures, no matter what their density.

For most purposes the definition of the Joule-Thomson effect given in equation (6) is the most convenient; but if we prefer to define it by reference to an adiabatic expansion and let μ be the fall of temperature per unit fall of pressure, the reasoning of § 2 applied to an infinitesimal fall of pressure gives us

$$\mu C_p = \rho \quad (15)$$

Without numerical data on the quantities involved in equation

(8) it is not obvious what the sign of μ or ρ will be, to say nothing of magnitude.

But there is another expression for ρ , which may easily be shown to be equivalent to equation (8); it is *

$$\rho = -\frac{\partial}{\partial p} \left(pv \right)_\theta - \left(\frac{\partial \epsilon}{\partial p} \right)_\theta \quad (16)$$

This equation, while useless for computation, is quite clear physically. Of the terms on the right side, the first is the external work done by the fluid, and the second is the increase of its internal energy, both per unit *fall* of pressure at constant temperature and measured for unit mass.

The second term may also, though rather loosely, be called the internal work, and it includes the work done against the cohesive forces, self-attraction, or internal pressure during the expansion of the fluid with falling pressure. Equation (16) is therefore in the simple form

$$(\text{heat put in}) = (\text{work given out}) + (\text{increase of internal energy}).$$

Suppose, to take an extreme case, that the air reaching the valve has been cooled all the way to its normal boiling point by the cold derived from boiling off some of the liquid air which surrounds the lower turns of the worm. When it is released through the valve, its increase of volume is greater than if it started under the same pressure at a higher temperature, since its initial density is greater at the low temperature. Hence both the external and the internal work might be expected to be greater and the absorption of heat greater than if the expansion started at a higher temperature. We could not tell from equations (8) or (16) just the numerical value of ρ or μ without data on the properties of air down to its boiling point, and these are lacking. We are certain, however, by the general reasoning of §§ 2 and 3, that the greater cold due to starting the expansion at a very low temperature produces just enough more liquid in the jet to offset the liquid boiled away in cooling the air down to this very low temperature before it arrives at the valve.

* See note at the end of this paper.

As for the process that goes on actually inside the nozzle, valve, or porous plug, complicated as it is by kinetic energy of eddy currents which has not yet been dissipated, it can not be followed in detail. Pressure and temperature cease to have any meaning under such turbulent conditions. Whether the jet of air from the valve is to be looked upon as liquid evaporating or gas condensing is somewhat a matter of words and can not in practice be decided from the appearance of the jet. The advantage of applying thermodynamics to such problems as those discussed in this paper is that it frequently, as in the present case, enables us to pass over intermediate details and arrive, notwithstanding, at results which are as trustworthy as the two laws of thermodynamics and the experimental data we have to use.

The thermodynamic theory of liquefiers in which the expansion valve is replaced by a motor is somewhat less simple than that of the Hampson liquefier, because even if the expansion in the motor be assumed to be isentropic, the interchanging process which goes on in the regenerator is essentially irreversible. The allowance to be made for the increase of entropy involved is somewhat uncertain, and in obtaining numerical values for x one is driven to the use of successive approximations, so that the computations are more laborious. Sufficient data are available in the case of air to permit of an approximate solution under practicable initial conditions.

If a turbine is to be used as the motor, its design is subject to the same general principles as that of a steam turbine. With an initial pressure of 40 atmospheres and an initial temperature of $16^{\circ}\text{C}.$, the exit velocity of the mixture of liquid and gaseous air from a Laval nozzle would be considerably less than in the steam turbine, and the kinetic energy per cubic centimeter not very different from that in the Laval steam turbine. It may therefore be practicable to use a simple, single stage, impulse turbine as a substitute for the expansion valve of the Hampson liquefier.

The theory of this type of liquefier will be given in a subsequent paper, when it is hoped that some experimental results may also be communicated.

NOTE ON THE EXPRESSIONS FOR ρ

Equation (16) or

$$\rho = - \frac{\partial}{\partial p} \left(pv \right)_\theta - \left(\frac{\partial \epsilon}{\partial p} \right)_\theta \quad (16)$$

is much the clearest mathematical expression of the Joule-Thomson effect ρ . For it is merely a statement that if unit mass of the fluid expands so that its pressure falls by unity, the quantity of heat that must be supplied, if the temperature is to be kept from falling, is equal to the external work done by the fluid plus the simultaneous increase in its internal energy; and this, again, is merely a statement that the first law or principle of the conservation of energy is applicable to the process. The only peculiarity of the equation is that the external work done by the fluid in an infinitesimal expansion does not take the form $p\delta v$ which it has for a reversible expansion against a pressure equal to that of the gas. Instead, we have for the irreversible expansion through a porous plug, where the fluid enters the plug at one pressure and leaves it at a different pressure without doing any external work while in the plug, a quantity of work $\delta(pv)$ given out by the fluid.

To show that equation (16) is equivalent to equation (8) we may proceed as follows: If W represents work done on any system, Q heat given to it, and ϵ its internal energy, the first law states that in any infinitesimal change of state

$$\delta\epsilon = \delta Q + \delta W \quad (a)$$

The second law states that if the change is reversible

$$\frac{\delta Q}{\theta} = \delta\eta \quad (b)$$

where η , the entropy, is determined solely by the instantaneous state of the system and not by its past history, and where θ is the temperature on Kelvin's absolute thermodynamic scale. Since in a reversible expansion the work done on the fluid is $-p\delta v$, equations (a) and (b) give, as the combined expression of the two laws of thermodynamics when applied to reversible infini-

tesimal changes of state of a mass of fluid subject to no outside forces except an uniform pressure p , the equation

$$\delta\epsilon = \theta\delta\eta - p\delta v \quad (c)$$

upon which may be founded the whole of the thermodynamic study of fluids in equilibrium.

For an isothermal change in which the increase of pressure is δp , equation (c) becomes

$$\left(\frac{\partial\epsilon}{\partial p}\right)_\theta = \theta\left(\frac{\partial\eta}{\partial p}\right)_\theta - p\left(\frac{\partial v}{\partial p}\right)_\theta \quad (d)$$

By subtracting $\delta(\theta\eta - pv)$ from both sides of equation (c) we get

$$\delta(\epsilon - \theta\eta + pv) = -\eta\delta\theta + v\delta p \quad (e)$$

and since ϵ , η , and v are all completely determined by θ and p , the first member of (e) is a perfect differential and the equation is in the form

$$\delta\zeta = \left(\frac{\partial\zeta}{\partial\theta}\right)_p\delta\theta + \left(\frac{\partial\zeta}{\partial p}\right)_\theta\delta p$$

where

$$\zeta = \epsilon - \theta\eta + pv; \quad \left(\frac{\partial\zeta}{\partial\theta}\right)_p = -\eta; \quad \left(\frac{\partial\zeta}{\partial p}\right)_\theta = v$$

But since the order of differentiation with regard to two independent variables is immaterial, it follows that

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial\zeta}{\partial\theta}\right)_p\right]_\theta = \left[\frac{\partial}{\partial\theta}\left(\frac{\partial\zeta}{\partial p}\right)_\theta\right]_p$$

or

$$-\left(\frac{\partial\eta}{\partial p}\right)_\theta = \left(\frac{\partial v}{\partial\theta}\right)_p \quad (f)$$

Substituting from (f) in (d), we have

$$\left(\frac{\partial\epsilon}{\partial p}\right)_\theta = -\theta\left(\frac{\partial v}{\partial\theta}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\theta \quad (g)$$

and substituting from (g) in (16), we have

$$\rho = -\frac{\partial}{\partial p} (pv)_\theta + \theta \left(\frac{\partial v}{\partial \theta} \right)_p + p \left(\frac{\partial v}{\partial p} \right)_\theta$$

or since

$$\frac{\partial}{\partial p} (pv)_\theta = p \left(\frac{\partial v}{\partial p} \right)_\theta + v$$

we have finally

$$\rho = \theta \left(\frac{\partial v}{\partial \theta} \right)_p - v \quad (8)$$

This is equation (8), which has thus been obtained by a simple series of operations from equation (16). It expresses the value of the Joule-Thomson effect in terms of directly measurable quantities—the specific volume, temperature and rate of thermal expansion at constant pressure—and is therefore convenient for computing purposes. Equation (16), on the other hand, has the advantage that its correctness is obvious to anyone familiar with the law of conservation of energy, as soon as the nature of the process to which it refers, namely, expansion through a fine-grained porous plug, is understood. For qualitative reasoning, equation (16) is therefore frequently preferable to equation (8).

WASHINGTON, May 15, 1909.

